19. FRENCH REPUBLIC
NATIONAL INSTITUTE
OF INDUSTRIAL PROPERTY
PARIS

11. **Publication Number:** **2 815 352**

21. **National Registration Number:** **00 13094**

51. **Int Cl: C 08 J 5/08,** C 08 J 5/24, A 61 C 13/03, A 41 C 3/00, 3/10, B 29 C 70/06, 70/42

12.

PATENT APPLICATION

22. **Filing date:** 12.10.00

30. **Priority:**

43. **Date of publication:** 19.04.02 Bulletin 02/16

56. **List of cited documents in the preliminary research:** Please, report to the end of the present document

60. **Reference to other related national documents:**

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54. COMPOSITE MATERIAL, ITS FABRICATION PROCESS AND ITS USERS.

57. The invention concerns a composite material, its fabrication process and its applications.

The composite material of the invention is a fibre composite material, whose non-cured resin-impregnated fibres are wrapped in a sheath, which maintains and compresses them to the desired shape. The sheath is made of flexible material and is totally-enclosed.

The invention is applicable in the production of bra underwires or prosthetic, in particular dental, elements.

The invention concerns a composite material, a method for making this composite material, as well as the use of this composite material for making prosthetic, in particular dental, elements and bra underwires. It also concerns a method for making prosthetic, in particular dental, elements and a device for making prosthetic, in particular dental, elements.

Composite materials are materials whose matrix is a polymerisable resin, consisting of glass, quartz, or ceramic mineral fillers in the form of particles of varying shape and size. Fibre composite materials are a specific type of composite materials. Fibre composite materials are also made of a polymerisable resin matrix but the filler is not made of particles of varying shape and size, rather of discontinuous fibres, or better still, continuous, woven, plaited, or unidirectional fibres.

Fibre and non-fibre composite materials are used in many industrial fields because of their mechanical strength and low weight.

For example, in the chemical industry many components made of composite material are necessary for their excellent mechanical, chemical, etc., strengths.

Besides, current trends in dentistry at the present time lean towards the elimination of metal use, in order to avoid problems linked to corrosion, which is caused by galvanic currents created by metals and their alloys.

Therefore, composite materials, whose matrix is of polymerisable resin, consisting of glass, quartz, or ceramic mineral charges in the form of particles of varying shape and size and not in the form of fibres, are aesthetical, functional, and economical alternatives to dental reconstructions using precious and non-precious metals and covered or non-covered with pure ceramic.

However, these composite materials whose matrix is of polymerisable resin, consisting of glass, quartz, or ceramic mineral fillers in the form of particles of varying shape and size, also known as cosmetic composite materials, must be strong enough to resist forces applied during mastication. It is therefore necessary to create a rigid armature on which cosmetic composite materials are then applied and to which they adhere.

This armature, which acts as a mechanical support, is made of fibre composite

materials described above.

In the women's lingerie industry, underwire bras are equipped with cups comprising metal underwires.

However, metal underwires twist when washed, rust, pierce fabrics, lose their elasticity with time, and break because of metal fatigue.

As a result, for many years, bra manufacturers have wanted to replace metal underwires with underwires made of different materials, which would not have the same disadvantages.

At present, fibre composite materials in the form of woven or plaited fibres, which are already pre-impregnated with non-cured polymerisable resin or which can be immersed at the time of use in non-cured polymerisable resin, are being used. They are moulded to the desired form and then the resin is hardened (polymerised), either by heat when it is thermosettable, or by light when it is photopolymerisable, and in some cases both methods are used.

These resin-impregnated products have several disadvantages:

- they present themselves in the form of fibre tufts or laps, impregnated with non-cured resin, which has the consistency of honey. Their manipulation is therefore difficult, as they are sticky, doughy, tacky, and hard to implement.
- when manipulated, fibres part, slide against one another and lose their cohesion, therefore making the mechanical properties of the item to be obtained uncertain and non-reproducible.
- the polymerisation of certain resins is inhibited when contact with air occurs during the polymerisation of the item to be obtained, resulting in the formation of a surface layer of viscous and sticky looking non-cured resin. This surface layer appears on the surface of the finished product after the composite material has hardened. This non-cured resin layer, even if very thin, must be removed. This can be done through a grinding process, which takes place until the polymerised resin is reached. The resin must then be re-polished, adding new steps to the fabrication of the item.

But most importantly, the making of curved parts or complicated forms in these fibre composite materials requires specific and very expensive equipment, which can

only be used for large series. At present, the fabrication of complex curved parts, such as springs, is difficult and very expensive.

These days, the making of thermosettable composite curved profiles is implemented by curved pultrusion, called pull forming, which allows the making of simple shapes with specific equipment designed for a particular form. This is very costly and can only be used for large series.

Pull forming is a process consisting in extracting resin-impregnated fibres and shaping them to their required shape.

However, complex forms such as springs cannot be obtained by this method.

Another existing technique is called bag moulding, which consists in enclosing resin-impregnated woven or non-woven fibre laps between two polyethylene sheets, or another polymeric material, and pressing them in a mould in order to obtain an item. However, once again, this extensively used technique does not allow the making of curved profiles such as springs. In the above and following texts, the terms "polymerisable", "hardenable", "curable" and their grammatical derivatives and variations will be used indistinctly, referring to the hardening of the resin.

The invention aims to overcome the weaknesses of the prior art, offering a fibre composite material, which enables the making of very complex curved items. These items will posses consistent and reproducible mechanical properties, whether industrially made or made on-demand, and their application will be made easy.

The composite material of the invention comprises fibres impregnated with a resin, which polymerises in reaction to one or several stresses. The invention is characterised by the fact that:

- fibres are in the form of sensibly unidirectional parallel fibres, tufts, twists, plaits, woven or non-woven slivers or woven or non-woven fibre boards.
- non-cured resin-impregnated fibres are placed in a sheath, which compresses the resin-impregnated fibres and gives them the desired form.
- the sheath containing the non-cured resin-impregnated fibres is made of flexible material, in order to take the form of the item to be obtained.
- the sheath is closed after the fibres and the resin have been introduced.

Fibres are ideally selected from the group consisting of: glass fibres, quartz fibres, silica fibres, aramid fibres, Kevlar fibres, polyethylene fibres, carbon fibres, or their blends.

Some of the most popular fibres are zirconium-based glass fibres.

In this case, the zirconium oxide contained in the glass used to make the fibres represents between 16.8% and 17.1% of the total weight of the glass.

One of the characteristics of the composite material of the invention is that the curable resin polymerises when in contact with heat and/or light.

Another very satisfactory curable resin is Bis-GMA resin.

One of the advantages of the composite material of the invention is the fact that fibres represent 40% to 80% of its total (fibres plus polymerisable resin) volume.

As for the sheath, it is preferably made of transparent polymeric material. It can also be made of polymeric material resistant to temperatures greater than about 100°C. The sheath is preferably made of air-tight polymeric material.

If possible, the sheath is also made of thermoshrinkable polymeric material.

Preferably, the composite material of the invention will be wrapped in a light-sealed packaging material.

The composite material of the invention can be used for making prosthetic, in particular dental, elements.

In this case, the inventive method for making prosthetic, in particular dental, elements comprises the following steps:

a) forming the composite material of the invention, inside its sheath, to the shape of the prosthetic element to be obtained.
b) polymerising the resin by applying suitable stresses.
c) removing the sheath.
d) eventually, machining the prosthetic element obtained.

Another inventive method for making prosthetic, in particular dental, elements comprises the following steps:

a) placing the impression of the prosthetic element to be obtained on the rotational axis.
b) cutting at least one extremity of the sheath of the composite material of the invention.

c) winding up the resin-impregnated fibres coming out of the sheath's extremity onto the impression of the prosthetic element to be obtained. This winding up takes place through the rotation of the rotational axis until the desired form for the prosthetic element is achieved.

d) polymerising the resin by applying suitable stresses on the impression.

e) separating the prosthetic element obtained from the impression.

f) removing the sheath.

g) eventually, machining the prosthetic element obtained.

The invention also offers a device for making prosthetic, in particular dental, elements, which is characterised by the following:

- a supporting base holds a horizontal rod. This rod is able to move forward and backward and from the left to the right on the supporting base and can be fastened onto this base.
- a first vertical rod is fastened at its lower end by a clamping screw to one end of the horizontal rod and is able to move from the left to the right and can be immobilized on this horizontal rod by the clamping screw. This first vertical rod holds a device at its upper end enabling the rotation of the rotational axis fixed to it. The rotational axis is placed in the extension of the device and is equipped with a jaw that enables the fixing and removal of the impression of the prosthetic element on the rotational axis.
- a second vertical rod is fastened at its lower end to the other end of the afore-mentioned horizontal rod with a clamping screw, allowing it to move to the right and left, forward and backward, and also allowing it to be immobilized on this horizontal rod. This second vertical rod holds at its upper end a ball bearing device, receiving a horizontal free rotational axis. This horizontal axis holds at its end, facing the rotary axis supported by the first vertical rod, a stop plate which is perpendicular to the horizontal axis. Its other end holds a locking device allowing the mobile horizontal axis to be locked in the desired position.
- the stop plate and the rotary axis are aligned so that the impression of the prosthetic element to be obtained can be placed between them.

The stop plate which enables the horizontal axis to lock in the ball bearing device

can be of different forms. It is preferably detachable. Therefore, the stop plate will have parallel faces.

The stop plate allowing the horizontal axis to lock in the ball bearing device can also be equipped with a centring and positioning cone, in order to position the impression of the prosthetic element to be obtained. It is also detachable.

The stop plate can also have the form of a truncated cone.

It can also have the form of a hemisphere.

In all manufacturing methods, the stop plate is preferably made of elastic malleable material and/or non adherent to fibre or non-polymerised resin material.

Accordingly, the jaw enabling the impression to be fixed and removed from the prosthetic element to be obtained can have different forms.

Therefore, the jaw can be a device which enables to insert the complete external surface of impression's end.

It can also be a device which enables to partially clamp the surface of an impression's end.

It can also be a device in the form of a cone, whose sharp end can be inserted by compression into one section of the impression's end.

The jaw will preferably be removable and equipped with a clamping screw to enable its fastening and locking on the rotational axis.

The composite material of the invention can also be used for making bra underwires.

The invention concerns therefore also bra underwires, characterised by the fact that they can contain the hardened composite material of the invention.

The invention concerns another method for making the composite material of the invention and is characterised by the fact that it includes the introduction by extrusion under pressure of hardenable non-cured resin-impregnated fibres in a sheath and the sealing of the open extremities of the sheath by stapling or thermowelding.

One of the favourite methods for making the composite material of the invention comprises the following steps:

a) introducing a piece of rigid and hollow tube in one end of a longitudinal sheath. This

tube's external section must be approximately the size of the sheath's internal section. The other part of the rigid and hollow tube must be left outside the sheath.

b) fixing the hollow tube in the sheath by any suitable means.

c) introducing a rigid and tension-resisting wire inside the sheath. This wire must have a section enabling it to slide freely inside the sheath and must be longer than the length of the sheath, and coming out of the sheath's two ends.

d) fixing the other end of the rigid wire coming out of the rigid tube to one end of the fibre bundle coming out of the sheath.

e) impregnation of the fibres with the hardenable non-cured resin, before their introduction inside the sheath.

f) introduction of the hardenable non-cured resin-impregnated fibres inside the sheath by pulling on the end of the wire coming out of the sheath.

g) sliding along the sheath, during the introduction of the resin fibres, of a hollow element, whose shape and internal dimensions correspond to the shape and external dimensions of the non-hardened composite material to be obtained.

The sheath is preferably made of thermoshrinkable material and is heated after resin-impregnated fibres have been introduced and before, at the same time, or after the hollow element is slid to give the item its required form.

The invention will be better understood, and its aims, characteristics, details, and advantages will appear more clearly by reading the following explanatory description, referring to the appended figures:

- figure 1 represents a cross-section view of a first method for making the composite material of the invention.

- figure 2 represents a top view of a second method for making the composite material of the invention.

- figure 3 represents a cross-section view from axis III-III of the composite material of the invention represented in figure 2.

- figure 4 schematically represents a cross-view section of a first prosthetic dental element made in the composite material of the invention.

- figure 5 represents a schematic cross-view section of a second prosthetic element

made in the composite material of the invention.

- figure 6 represents a schematic cross-view section of a third prosthetic element made in the composite material of the invention.

- figure 7 represents a first implementation method of the composite material of the invention.

- figure 8 represents the prosthetic element obtained by implementing the composite material of the invention as shown in figure 7.

- figure 9 represents the first step for making a reinforcement in the composite material of the invention.

- figure 10 represents an intermediate step for making the reinforcement in the composite material of the invention, whose first fabrication step is shown in figure 9

- figure 11 schematically represents the inventive device used for making a prosthetic element with the composite material of the invention.

- figure 12 schematically represents a first variant of the stop plate used in the inventive device.

- figure 13 schematically represents a second variant of the stop plate used in the inventive device.

- figure 14 schematically represents another method for implementing the composite material of the invention in the making of prosthetic elements.

- figure 15 represents still another method for implementing the composite material of the invention in the making of prosthetic elements.

- figure 16 schematically represents a method for making the composite material of the invention.

- figure 17 schematically represents a method for making the composite material of the invention.

- figure 18 schematically represents a third variant of the stop plate used in the inventive device.

- figure 19 schematically represents a fourth variant of the stop plate used in the inventive device.

- figure 20 schematically represents a first variant of the jaw used in the inventive

device.

- figure 21 schematically represents a second variant of the jaw used in the inventive device.

- figure 22 schematically represents a third variant of the jaw used in the inventive device.

The invention solves the problems that composite materials of the prior art had, by offering an easy to manipulate composite material, in which fibres are homogeneously linked, giving the item homogeneous mechanical properties and making items of all shapes possible.

Indeed, as shown in figure 1, the composite material of the invention is composed of fibres 1, which are either unidirectional and parallel or in the form of tufts, twists, plaits or woven or non-woven slivers. These fibres (1) are impregnated with hardenable non-cured resin (2) and wrapped in a sheath (3), which shapes both the fibres and the resin to the desired form. The fibres (1) and the resin (2) form in their sheath (3) a homogeneous group which does not lose its homogeneity when handled, thanks to the sheath (3) which prevents the fibres to part and slide one against another. Also, because the cured resin is not sticky anymore, manipulating the composite material of the invention is easy.

The composite material of the invention enables the item to have homogeneous and reproducible mechanical properties. Almost any shape, no matter how complex, can be obtained with reproducibility and reliability.

The sheath (3) covering the resin-impregnated fibres must be made of flexible material in order to shape the composite material of the invention as required.

Obviously, the sheath (3) will be closed at both ends to prevent fibres 1 and the non-cured resin 2 from coming out of the sheath (3) during the handling of the composite material. It also helps maintaining the homogeneity of the fibres 1 and the resin 2 during their handling and subsequent hardening.

The fibres (1) can be all sorts of fibres which are adapted to the mechanical, optic, and elastic, etc., properties of the item to be obtained.

The resin (2) will be hardenable by the application of one or several stresses, which

will fix the shape of the item to be obtained.

The resin (2) can thus be a thermosettable resin (hardenable by heat). It can also be a photocurable resin (hardenable by light exposure). At last, it can be both photocurable and thermosettable.

When the resin is photocurable, the sheath (3) must be made of transparent material with an appropriate wave length. When the resin is thermosettable, the sheath (3) must be made of material resistant to the temperature of resin hardening. As explained above and in the following text, the terms hardening, polymerisation, curing and their grammatical derivatives will be used indistinctly and will designate the hardening of the resin (2). In the case of photocurable and thermosettable resins, the sheath (3) will be both in a transparent material resistant to certain light wave lengths and in a material resistant to the temperature of resin hardening.

While in figure 1 the composite material of the invention is represented as composed of resin-impregnated longitudinal fibres, figures 2 and 3 represent another method of making the material of the invention.

As shown in figure 2, the composite material of the invention can also be in the form of woven or non-woven resin-impregnated fibre sheets. Their shape can be rectangular, circular, oval, etc. Fibres are wrapped inside the sheath (3), which completely adheres to the shape of the sheets. Here as well, the sheath (3) is closed on the sides. The fibres (1), the resin (2) and the sheath (3) will have the same properties than if longitudinal fibres, described earlier, were used. Figure 2 represents a top view of the composite material of the invention in the form of sheets, whereas figure 3 represents a cross section view of the composite material of the invention consisting of a hardenable non-cured resin(2)-impregnated woven or non-woven fibre (1) sheet, wrapped in a sheath (3) closed on the sides.

For all fabrication methods of the composite material, when the resin (2) is photocurable, the composite material of the invention must be wrapped in an opaque packaging material in order to prevent polymerisation of the resin during its storage and/or its transport. Such a packaging material could be aluminium.

As previously explained some resins are oxidation-sensitive and sustain inhibition

in regards to their polymerisation ability. Therefore, the sheath (3) will preferably be made of air-tight material to prevent oxidation during transport or storage of the composite material of the invention.

Although the variety of items and uses of the composite material of the invention is very wide and the fact that it can be used in all industry fields, a common field for using the composite material of the invention is for the making of prosthetic, in particular dental, elements.

In fact, these prosthetic elements must be made on demand and cannot be industrially manufactured.

For the making of dental prosthetic elements, the preferred fibres composing the composite material of the invention are glass fibres, quartz fibres, silica fibres, aramid fibres, Kevlar fibres, polyethylene fibres, carbon fibres, and blends of these.

Preferably, glass fibres will be used because they have the advantage, in particular over carbon fibres, to have a colour closer to that of the natural teeth. Indeed, glass fibres have an off-white colour, which makes them particularly adapted for dental use.

Preferred glass fibres for the making of prosthetic elements are zirconium oxide-based glass fibres. In fact, such glass fibres are radiopaque, that is to say visible on dental x-ray.

Components of preferred glasses include zirconium oxide. In fact, the latter dissolves at the same time as other glass components during the fabrication of the glass, which is transformed into fibres.

Thereby, the zirconium oxide contained in the glass used to make the fibres represents between 16.8% and 17.1% of the total weight of the glass.

Thanks to their zirconium oxide content, these glass fibres are particularly adapted for dental use.

Indeed, saliva makes the buccal cavity a more corrosive environment than marine air, which is the reference environment for corrosion resistance tests on industrial products.

The salivary pH of one individual can be alternatively acid or basic. Any object in permanent contact with saliva is in a 100% humid environment, tempered at 37°C and

subjected to a hydrolysis corrosion phenomenon. Furthermore, this environment contains aerobic and anaerobic bacteria, capable of secreting all sorts of alkanes, ketones, and other substances which are also corrosive.

Glass fibres containing zirconium oxide are preferred in the composite material of the invention because of their great resistance to acid and alkaline substances, made possible by their zirconium oxide proportions. Their resistance is ten times superior to that of glass fibre containing no zirconium oxide. They are more resistant to hydrolysis in humid environment and also have better mechanical properties, especially greater fatigue strength, which makes them particularly adapted for dental reinforcements.

Finally, these zirconium oxide enriched glass fibres have an average diameter of 14 to 20 µm and are able to break down into particulates while keeping a size superior to 3 µm when grinded by machining or attacked by hydrolysis, which makes them non-breathable. This is very important for a material dedicated to stay in the mouth for years and also for the health of professionals who work, machine and grind the items obtained from the composite material of the invention.

Particularly appropriate fibres are the ones sold under the brand "Cem-Fibres" by VETROTEX, a subsidiary company of Saint Gobain.

The resin (2) used for the composite material of the invention can be any resin, which is polymerisable by application of one or several stresses.

Preferably, this stress will be heat or light, either visible, infrared or UV light.

It can also be a resin both photocurable and thermosettable. An appropriate resin (2) that can be used in the composite material of the invention can be chosen amongst epoxy, polyester, vinylester resins, which are thermocurable resins, or amongst the polymetacrylate or diurethane resins, which are both photopolimerisable and thermopolimerisable, or derivatives of these.

The resin (2) will preferably have a viscosity ranging from 400 to 800 Pascal seconds. Viscosity can be adjusted by the addition of fillers, such as quartz, barium glass, ceramic, or other particulates, whose size is comprised between 0.3 and 10 µm.

This resin's modulus of elasticity or Young's modulus should range between 30 Gpa and 150 Gpa.

A preferred resin for the making of dental prosthetic elements is a Bis-GMA resin. The latter is used in dentistry for the prophylactic sealing of pits and fissures and is known as “flowable composite”. It is sold under the brands "HELIOSEAL F" by Vivadent or CONCISE WHITESEALANT by 3M.

The choice of this resin is justified by at least two different reasons.

The first reason is that Bis-GMA resin has the same chemical nature as the resin used in the cosmetic composite material, which will later be attached to it. This allows a chemical bond, that is to say a fusion between the two materials, which eliminates decoalescence problems between these materials.

The second reason is the fact that Bis-GMA resin shrinks while hardening. The greater the amount of resin, the more the resin will shrink.

This shrinkage had until now been considered as the major disadvantage of filling composites, which after polymerising decrease and create spaces between the composite and the sides of the cavity holding them, possibly causing salivary infiltration and tooth decays.

The composite material of the invention takes advantage of this shrinkage, as it favours the sliding and removal of the hardened part from its sheath.

In this purpose, the volume of fibres in the reinforcement will preferably range from 40 to 80% of the total volume of the fibres and the resin. Preferably, the volume of resin in the composite material will range from 40 to 50%.

The prosthetic element obtained must have the following minimal mechanical properties:

- flexural strength: more than 1000 Mps
- bending modulus: more than 40 Gpa

The sheath of the composite material of the invention is a sheath made of flexible polymeric material, able to be shaped to the desired form. Amongst suitable polymeric materials are: polyolefin, polyvinyl chloride, polyethylene, polypropylenes, silicones, siliconised rubbers, etc. As previously explained, the sheath (3) is air-tight and if used with a thermocurable resin must also be able to resist the polymerising temperature of the resin.

The sheath will generally have to resist a temperature above 100°C, and preferably above 140°C.

When the resin (2) is photocurable, the sheath has to be transparent to a certain wave length light.

The ability of the composite material of the invention to be formed inside its sheath will be determined by the choice of polymeric material of the sheath, as well as the thickness of the sheath. However, the sheath must be thick enough not to break during the forming of the prosthetic elements to be obtained. Therefore, the sheath's thickness will preferably be comprised between 0.2 mm and 1.5 mm.

The sheath will preferably be thermoshrinkable, which has the advantage of compressing and condensing the composite material during the polymerisation (hardening), optimising thereby the mechanical properties of the prosthetic element obtained. Preferred thermoshrinkable sheaths are made of modified polyolefin material, irradiated polyofelin, silicone, polytetrafluoroethylene (PTFE), or polypropylene.

The sheath will generally be made of polymeric matter, such as polyvinyle, polyvinyl chloride (PVC), polyethene, polypropylene, polyurethane, polyolefin, polyethene terephtalate (PET), polytetrafluoroethylene (PTFE), siliconised rubber, elastomer, silicone, and their derivatives.

The composite material of the invention is thus composed of fibres (1), impregnated of hardenable non-cured resin (2), introduced in a sheath (3), made of flexible material ready to be shaped. This fibre composite material is introduced in the sheath (3), for example by extrusion under pressure, in order to obtain an air bubble free product and with constant resin and fibre proportions. The resin must be non-cured and for that reason the sheath must be transparent to certain wave length light and/or resistant to the hardening temperature of the resin, as described above and depending on the type of resin used.

Furthermore, when the polymerisation of the resin is inhibited by air contact oxidation, which is the case for the preferred Bis-GMA resin, in particular for dental use, the sheath will protect the resin from such air contact. In fact, polymerisation of the resin occurs while the fibre composite material is still inside its sheath. There is no air contact

during the resin polymerisation.

To prevent the composite material to oxide or come out of its sheath, the sheath will be closed at both ends by thermowelding or mechanical stapling. It will then be adjusted to the required length.

When the composite material has the shape of a plate, the sheath is thermowelded to the desired shape and then cut, as shown in figure 3.

In order to prevent the pre-curing (pre-polimerisation) of the resin during the storage or transport of the composite material, the latter is wrapped in an opaque packaging material, in addition to its sheath. A material that can be used for the packaging is aluminium, for example.

As explained earlier, the composite material of the invention is used more particularly in dentistry, in fields such as endodontics, prosthetics, orthodontics, and periodontics.

It can be used in particular for making orthodontic or periodontic dental splints, prosthetic crown armatures or dental bridges, reinforcements, or for restorative dentistry work, such as corono-radicular reconstructions (also called posts).

However, the composite material can be used to make other prosthetic elements than dental, as experts will notice.

Another application field of the composite material is the making of corrosive resistance items, such as the ones used in the chemical industry. The composite material of the invention can be used to make complex curved items, such as springs.

This will be obtained by winding the composite material of the invention in its sheath around a mandrel of the dimensions required for the springs, hardening of the resin by application of the appropriate stress on the composite material in its sheath, removal of the hardened composite material from the mandrel and finally removal of the sheath.

Another field of application of the composite material, that is particularly preferred, is the making of bra cup underwires.

In fact, bra manufacturers have wanted for many years to replace metal bra underwires, which twist when washed, rust, pierce fabrics, lose their efficiency with time

and break from metal fatigue.

Numerous requirements exist: bra cup underwires must resist the very corrosive washing agents, must mechanically resist the washing machine (50 washings test) at a temperature of 50°C, must keep their elasticity throughout the years and be non-toxic and non-allergenic to the skin.

In addition, there are 20 sizes per model and more than 50 models changing with the new collections. The price of dies makes the fabrication of bra underwires by moulding injection too expensive.

Besides, the bra underwire's shape is asymmetrical and non-nestable: it is not possible to cut them out in plates because it would lead to unacceptable material losses.

The composite material of the invention allows the making of underwires in an affordable manner while overcoming the metal underwires disadvantages cited above.

In that case, the composite material fibres (1) will be chosen amongst carbon fibres, glass fibres or aramid fibres, such as Kevlar.

The resin (2) will be chosen amongst polyester, vinylester and epoxy resins which are thermosettable.

The sheath (3) will preferably be of a polymeric material such as polyethylene, polyeturethane, polypropylene, PTFE, silicons or their derivatives. The sheath (3) can be transparent or opaque. Besides, its colour can be in harmony with the fabric covering it.

Therefore, in order to make bra underwires, the non-cured composite material of the invention in its sheath will be wound around a mandrel having the form of two underwires facing each other. Once the winding process has finished, the mandrel with the composite material to be wound will be placed in a heated chamber where the material will harden.

The mandrin, which is covered with cured composite material in its sheath, is then placed on a device consisting of two diamond slitting wheels, which horizontally cut the composite, liberating the finished underwires. For this purpose, the mandrel comprises two slits allowing the diamond wheels to move.

The composite material of the invention can be used for making, in a very affordable way, bra cup underwires in a composite material, which has all the required

properties. In fact, mandrels made with the composite material of the invention can be designed as fixed nucleus. These will be able to receive the different shapes to be obtained, which are removable. The cost price for making them by mechanised welding or by machining as described above is incommensurable compared to injection moulding.

Besides, underwires made from the composite material of the invention do not need to be painted like metal underwires of the prior art, which were painted in order to prevent oxidation and corrosion in washing liquors as well as to enhance the comfort of the user.

At the moment, metal underwires' ends are painted with a thick plastic paint attenuating their asperities, which incidentally reappear throughout time and washes and which can hurt the user or pierce the fabric after the paint has peeled off. This also enables the differentiation between left cup underwires and right cup underwires, as both ends are coated with different colour paints.

The bra underwires obtained with the composite material can be painted in the same way, at the ends. However, advantageously, in order to distinguish left from right underwires, their ends are covered with thermoshrinkable plastic caps between 1 and 2 mm thick. The thermoshrinkable plastic material will then be heated in order to round off the ends. These caps will of course be of different colour as required.

These operations can be entirely automated and suppress painting steps, which represents an economical advantage as well as improved security and environment, as no paint solvent vapours are produced.

The composite material of the invention can be made, as already explained, by introducing resin-impregnated fibres inside their sheath, by a pressure-extrusion process. The invention however offers a way to introduce these fibres in their sheath. The principle of this process, as shown in figure 16, consists in introducing the resin-impregnated fibres (1) inside their sheath (3) by pulling them inside and through the sheath (3) with a fibre pull-out (40 in figure 16).

More precisely, and as shown in figure 17, the method for making the composite material of the invention consists in introducing in one end of the sheath (3) a section of

a rigid hollow tube (41 in figure 17), whose external section is about the same size as the internal section of the sheath (3), the other section of the tube (41) coming out of the sheath (3). The rigid hollow tube (41) is fixed by any suitable means (42) to the sheath (3). The compression mean (42) can be a clamping collar for example. The hollow tube (41) is maintained in a horizontal position by any suitable means (43). An orifice (44) on the section of the tube (41) coming out of the sheath (3) allows the resin (2) to be introduced inside the hollow tube (41). The resin (2) is placed, for example, inside a tank (45) emerging through the orifice (44) in the tube (41). The fibre pull-out (40), which can be a metal or other material wire permitting the guidance and traction of the fibres inside the tube (41) and the sheath (3), is introduced in tube 41 and the sheath (3). The fibre pull-out comprises a section whose external dimensions are inferior to that of the internal section of the sheath (3) and of the tube (41) to be able to travel horizontally inside tube 41 and the sheath (3). The fibre pull-out (40) has a length superior to the total length of the tube (41) and the sheath (3). As shown in figure 17, the end of the fibre pull-out coming out of the tube (41) is attached to the fibres (1). It is then pulled by its end coming out of the sheath (3). The fibres (1) then enter the tube 4(1). They are impregnated with resin 2 when passing under the opening/orifice 44 and, covered with resin 2, they enter the sheath (3), where they are pulled until the required size of the composite material of the invention is achieved. In order to obtain a composite material with regular and homogeneous dimensions, the sheath (3) is also placed in a hollow element 45 sliding on the sheath and whose shape and internal dimensions correspond to that of the non-hardened composite material of the invention.

One of the favourite implementation method of the fabrication process of the composite material of the invention involves the sheath (3) being made of a thermoshrinkable material. In fact, it is then possible to choose a sheath, which has a section with internal dimensions superior to that of the composite material to be obtained, allowing the resin-impregnated fibres to enter the sheath, thanks to the fibre pull-out, more easily.

After the resin-impregnated fibres have been introduced inside the sheath and the fibre pull-out has been removed, and before, at the same time, or after hollow element 45 has

been slid, the sheath is heated, for example with a hot air blowing device. The sheath then shrinks around the non-cured resin-impregnated fibres to the desired dimensions and shape.

In order to better understand the object of the invention, several methods of implementation will now be described. These are purely illustrative and non-restrictive.

EXAMPLE 1: Direct shaping fabrication process of dental splints

The composite material of the invention is composed of parallel unidirectional longitudinal glass fibres. The glass used is made from zirconium oxide, such as glass manufactured under the brand Cem-FIL® by Saint Gobain. Fibres are impregnated with Bis-GMA resin and contained and maintained in a totally-enclosed sheath, which shapes them.

The composite material of the invention in its sheath is then shaped into the desired splint shape on a gypsum model, which is an impression of the patient's dentition.

As shown in figures 7 and 8, this shaping can be direct. In this case, the dentist or prosthetist receives the composite material in its sheath and wrapped in a light-sealed bag (in aluminium for example, in order to avoid the beginnings of photopolymerisation).

He or she chooses the preform or profile and length required. When opening the protective wrapping the composite material of the invention can present itself as a flexible tube, filled with non-cured resin-impregnated fibres and closed at both ends.

One end of the sheath (3 in figure 7), containing the non-cured fibre composite material, is fixed on the impression (5 in figure 7), and the resin-impregnated fibres contained in sheath (3) are formed on impression 5 to the desired shape.

It might be necessary to slightly pierce the sheath to create a vent, letting the contained resin flow out and gain in flexibility.

The composite material having been shaped, the resin at vent level polymerises. It becomes hard and cannot flow anymore. Both impression 5 and the composite material inside its sheath are then polymerised in a laboratory light-chamber and thermoset in a

100°C heated chamber for the necessary time to finish the hardening. The sheath (3) is then cut, removed and the splint (6 in figure 8) out of the sheath is then ready to be used. As a matter of fact, polymerisation occurs with the sheath still wrapped around the composite material, no superficial non-polymerised layer is present. It is therefore not necessary, as was the case with the method and composite material of the prior art, to remove this superficial layer.

It is possible to make a reinforcement of bridge in the same way used to make a dental splint.

Of course, these elements can also be made with a resin different from Bis-GMA, for example epoxy resin.

EXAMPLE 2: Indirect shaping fabrication process of dental splint

In the same manner as previously, the dentist or prosthetist receives the composite material in its sheath and wrapped in a light-sealed bag (in aluminium for example, in order to avoid the beginnings of photopolymerisation). He or she chooses the preform or profile and length required.

However, in this case, as shown in figure 9, the trial denture (7) of the desired dental splint is first made with wax on the gypsum impression (5) of the dentition. Then, an impression of the dental splint to be obtained is made by moulding the impression (5) with the trial dental in a transparent non-cured silicone mould. The transparent silicone is then hardened, the impression is removed, and the trial dental is separated from the silicone mould and the gypsum impression, with boiling water.

The composite material of the invention in its sheath is then placed in impression 8 of the silicone mould. As shown in figure 10, the gypsum impression (5), whose trial (7) has been removed, is then pressed again inside the silicone impression (9), which contains the composite material in the impression (8) of the splint to be obtained. The composite material of the invention in its sheath is then photopolymerised through the silicone mould (9) and removed from the mould. It is thermocured. The transparent

sheath is removed and the dental splint is completed.

It is possible to make half-rush dental splints, very precisely adapted, from a round sheath. It is also possible to make crown caps with preformed circular sheets.

EXAMPLE 3: Making of bridge reinforcement

As shown in figure 4, a bridge is made of a) two abutment elements (10 in figure 4), supported by machined teeth (11 in figure 4) on each side of an empty socket and b) a pontic 12 in figure 4, which replaces one or several missing teeth.

The bridge's final shape is obtained by applying a cosmetic composite material 13 on the composite material-made reinforcement. The cosmetic composite material constitutes the anatomy and colour of the abutment teeth and the missing teeth (14 in figure 4).

In order to make a bridge, it is therefore necessary to first make an armature or reinforcement. It is made as explained for the dental splint, from a gypsum impression of the patient's dentition.

The abutment teeth are shaped in a conic form to make the insertion and removal of the prosthetic element possible.

In order to make the armature (10, 12), it is necessary to first cover every cut tooth with a cap (10), the caps then being all linked to one another by a pontic (12). The making of these caps is complex: they must be completely covered with the fibre composite material; the thickness of the fibre composite material must be small on the neck and greater on the top; and the quantity of fibres must be constant.

Resin-impregnated glass fibre materials are currently available in the form of pastilles, which are applied by pressing on cut teeth. This system has two disadvantages: a hiatus remains on the teeth neck because of the resin's viscosity and the fibre tissue not being contained in an envelope, the thickness of the reinforcement obtained is irregular.

A resin-impregnated fibre tuft can also be used, but the fibres compressed on the surface and angles of the cut tooth might part under the effect of pressure. Besides, they

cannot cover the whole arrangement.

These two methods using a viscous and sticky material are difficult to implement and give inconsistent results.

With the composite material of the invention contained in a sheath, it is possible to make regular and precise caps, no matter the shape of the abutment tooth stump (11), with perfect control of their thickness and fibre orientation. This can be achieved with the indirect shaping fabrication process described in example 2 or by the method of cire perdue, using both the cap preforms (10) and pontic profiles (12) and juxtaposing and superposing some of the parts, cleared from their sheath, of the composite material of the invention, and sealing them to each other, as shown in figure 14.

However, the inventive method of fabrication can also be used. By using the inventive process, it is possible to make precise caps (10), perfectly wrapping cut teeth and whose thickness and fibre orientation are controlled.

Therefore, as shown in figure 15, the composite material of the invention, comprising unidirectional continuous fibres or fibres in the form of plaits, is used. At least one of the sheath's ends must be cut to enable the resin-impregnated fibres to come out and to wind around the abutment teeth 11. This is done on each of the two cut teeth or more precisely on the gypsum impression of the patient's two cut teeth 11 to obtain caps 10. Then, the sheath containing the composite material will be cut at both its ends as shown in figure 15 and the reinforcement arch 12' will be made, as shown in figure 15, in order to make the pontic draft.

In this fabrication process, the sheath is used to manipulate the composite material of the invention. More precisely, as shown in figure 11, a perfect gypsum replica (14) the cut tooth is made inside the mouth. Gypsum replica 14 is equipped with a metal fastening rod (15 in figure 11), which enables its repositioning in the global dental impression.

This impression (14, 15) is then placed on a mechanical, hand-operated, or electrical device, which winds it around itself like a spool. The dentist or prosthetist can then wrap the resin-impregnated glass fibres as they are coming out of the sheath by holding the sheath by its protected part and emptying the material as desired on model 14 of the cut tooth. A stop plate (27) leans against the free section of replica 14 in order to

maintain the composite material on this replica 14. When the result is satisfactory, the dentist or prosthetist polymerises the arrangement as described above.

The caps of the abutments or then linked to one another by the thickest reinforcement in the pontic. The extremities of sheath have been previously removed to enable its fastening to the caps, as shown in figure 15.

This pontic is made as described above, either in direct from a suitable profile, or by the method of cire perdue and moulding as described for dental splints.

A device for implementing the method of the invention particularly advantageous is a device such as the one represented in figure 11.

This device comprises a base 16 supporting a horizontal rod or post (17). Rod 17 is able to move forward to backward and from the left to the right on the socle 16. The rod 17 can be fastened at the desired position on the socle 16 by any suitable mean of fixation, as for example a clamping nut 18, 18'.

A first vertical rod or post (19) is fastened at its lower end to one end of rod 17 (on the right in figure 11) by a clamping screw (20). Vertical rod 19 can move on rod 17 from left to right and forward and backward. It can be immobilised on rod 17 by clamping screw 20.

Vertical rod 19 holds at its upper end a device (21) allowing the rotational axis (22) fixed to it to rotate. Rotational axis 22 is in the extension of device 21 and comprises a jaw (23, 23', 23'', 23''') enabling the fixation of the impression (14, 15) of the prosthetic element to be obtained.

The jaw can be any device allowing the prehension and fixation of the impression of the prosthetic element to be obtained on the rotational axis (22).

As represented in figure 20, the jaw can be a device (23') comprising at one end a hollow section (50) enabling the insertion by compression of the impression's end (15). The other end of the jaw has a hollow section (51), equipped with a fixation mean (52), which can be a screw, in order to fix the jaw (23') on the rotational axis (22).

The jaw can also be, as represented in figure 21, a device comprising at one end (50') a jaw-articulated device 23'' enabling the prehension and fixation of the extremity 15 of the prosthetic element, as well as a fitting/tightening device, such as a screw 53. Its

other end has a hollow section 51, equipped with a fixation mean 52 to fix the jaw 23' on the rotational axis 22.

The jaw can also be, as shown in figure 22, a device (23''') whose first end (50'') comprises a cone for fixing the extremity (15), while its other end is equipped with the same device (51, 52) described for jaws (23' and 23'').

A second vertical rod number 24 is fixed at its lower end by a clamping screw (20') to the free end of horizontal rod (17, on the left side in figure 11). The vertical rod (24) is mobile on the horizontal rod (17) from the left to the right, forward and backward, and can be immobilised on the horizontal rod (17) by a clamping screw (20'). Vertical rod 24 holds at its upper end a ball bearing device 25, receiving a horizontal axis 26. Horizontal axis 26 freely revolves inside the device 25 and can slide from left to right in this device. Horizontal axis 26 can be blocked in a horizontal position, but not rotating, by any appropriate means, such as a nut (20'').

The horizontal axis (26) faces and is aligned with the rotational axis (22) and holds at its end facing rotational axis 22 a stop plate (27, 27', 27'', 27'''), which is perpendicular to horizontal axis 26. The plate (27, 27', 27'', 27''') and the rotational axis 22 are aligned in order for the impression (14, 15, 14', 15', 14'', 15'') of the prosthetic element to position. The plate (27, 27', 27'', 27''') enables the impression (14, 15, 14', 15', 14'', 15'') of the prosthetic element to stay in place, while maintaining the composite material on the impression. It also allows the impression (14, 15, 14', 15', 14'', 15'') to rotate around itself thanks to rotational axis 22.

The plate (27) can be a parallel sided plate, as represented on figure 12, where the impression is now positioned, or it can have, if possible, a cone-shaped element (28) to allow the impression of the prosthetic element to be centred and inserted, as represented in figure 13, where it is number 27'. This plate can also have the shape of a truncated cone (27''), as shown in figure 18. Or it can have a hemisphere shape (27'''), as shown in figure 19.

In any case, the plate will preferably be made of flexible elastic material, which will not only enable the locking of the impression and that of the composite material on the impression, but also the covering of nearly the whole impression (14, 14', 14'').

In practice, the parallel sided stop plate (27) in flexible elastic material will preferably be used, as shown in figure 12, for teeth impressions 14, 15, such as incisor and premolar teeth. Stop plate 27', as shown in figure 13, and stop plate 27'', as shown in figure 18, will preferably be used for impression 14'', 15'' of large occlusal surface teeth. Stop plate 27'', as shown in figure 25, will be used in all circumstances, depending on its diameter.

Advantageously, stop plates 27, 27', 27'', 27''' will be made of non resin adherent material, whether the resin is cured or non-cured.

Rotational axis 22 can be motioned thanks to device 21, which can be an electrical motor or a crank.

It is then possible, with the inventive process and device, to make abutment tooth caps as well as pontics for bridge reinforcements.

EXAMPLE 4: Making of corono-radicular reconstitution reinforcements, known as intra-radicular posts.

A post is made of a glass fibre tube embedded in a cured resin matrix, as shown in figures 5 and 6 respectively.

This post 28, 28' is then, as shown in figures 5 and 6, placed in a gypsum impression 30 of the tooth stump to be reconstituted. As in the case of the bridge, a resin made of cosmetic composite material 13', 13 is then applied on the post to shape it to the desired tooth shape. When making these intra-radicular posts and as shown in figure 5, the resin of the material composing the post 28 can be different from reconstitution cosmetic resin 13'. This is then called heterogeneous restoration. However, in such a case, risks of decoalescence between the reconstitution cosmetic resin 13' and the post resin 28 exist.

It is therefore particularly wise in the context of the invention to use, as shown in figure 6, a cosmetic composite material and a fibre composite material of the invention, which contain a Bis-GMA resin. As a matter of fact, the post 28' is then made of a

composite material, whose resin is identical to the cosmetic resin 13'. This allows the making of tailor-made, monolithic, homogeneous reconstitution, whose elements chemically adhere to one another, which is a great advantage over heterogeneous posts and associated products, likely to dissociate, as shown in figure 5.

To summarise, the invention offers a fibre composite material contained in a sheath or envelope, which gives it the desired shape. Preferably, the fibres of the fibre composite material are zirconia-based glass fibres, whose properties are far superior to that of traditional glass fibres, such as resistance to acid and alkaline corrosives and to hydrolysis in humid conditions. They also have better mechanical properties, such as better resistance to fatigue and can be manipulated without any danger for human health. The resin matrix is preferably a Bis-GMA resin of the same nature as the sealing resin used to tie up the prosthetic element and the reconstitution cosmetic material together. Indeed, a genuine chemical adhesion can then occur between the prosthetic element and the cosmetic composites attached to it. The result is a homogeneous restoration with no risk of dissociation.

The method of fabrication and more precisely the presentation of the composite material of the invention in a transparent sheath enable the achievement of varied profiles and preforms, which can be used as is or transformed as required, and enable its photopolymerisation sheltered from oxygen, which reinforces its resistance to corrosion and makes the manipulation of these composites and their final machining easier.

As a matter of fact, in every fabrication process of the invention, the prosthetic element obtained can then if necessary be machined in order to polish it and perfect its final shape.

The composite material of the invention is less sensitive to corrosion, easier to implement and therefore cheaper than metals used thus far. It also has a better rendering than micro filled dental composites, whose mechanical properties are insufficient. As a result, the invention brings a solution to that problem and opens up possibilities for more aesthetic, more affordable prostheses than classic ceramic and/or metal prosthesis.

Furthermore, the mechanical behaviour of fibre composite materials, whose elasticity moduli are closer to that of the tooth, makes them less fragile than metal or

ceramic, which immediately transmit all forces, increasing risks of restored teeth breaking.

The reinforcements made of the fibre composite material of the invention are a happy medium between solidity, durability and aesthetic imperatives of the dental prostheses and enable treatments which are easier in mechanical and financial respects.

Of course, the invention is absolutely not limited to the fabrication methods described and illustrated in this document, which only stand as examples. Therefore, although the invention has been described in the examples referring to dental prosthetic elements, all other prosthetic elements can be made from the composite material of the invention, thanks to its biocompatibility with the human body.

Furthermore, as depicted earlier, it can be used in other industry fields, such as in the making of complex form profiles, such as fibre springs or bra underwires.

The invention possesses all the technical equivalents to the methods described above, as well as their combinations, when carried out in accordance with its spirit.